

## PATENT ABSTRACTS OF JAPAN

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## (54) METHOD OF PRODUCING CORROSION RESISTANT IRON MATERIAL

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a method of producing a highly corrosion resistant iron material which has high rust preventability without using and containing harmful chromium based compounds.

SOLUTION: A rust preventive coating composition containing (a) a compound having a phenolic hydroxy group and (b) at least one or more kinds of compounds selected from the group of silicates and the salts of silicic acid and having a siloxane bond and/or their condensations as essential components is applied to the surface of an iron material whose surface is coated with an undercoating agent essentially consisting of at least one kind of metal selected from zinc and aluminum, and hardening is caused by room temperature treatment or heating treatment, so that a corrosion resistant iron material is produced.

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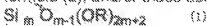
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## CLAIMS

[Claim(s)]

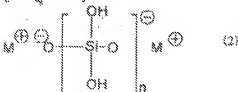
[Claim 1] A manufacturing method of corrosion-resistant iron material which applies a rustproof coating composition which uses the following (b) and (\*\*) as an essential ingredient to the iron-material surface which covered the surface by a primer which uses as the main ingredients at least one sort of metal chosen from zinc and aluminum, and it makes it come to harden by room temperature processing or heat-treatment.

(\*\*) a compound and (\*\*) which have at least one phenolic hydroxyl group in a molecule -- compounds which have at least one or more sorts of siloxane bonds chosen from a group of the silicate shown by a general formula (1), and the silicates which are shown by a general formula (2), and/or those condensates [Formula 1]



(R is a hydrogen atom and the basis chosen from a group of a univalent hydrocarbon group among a formula, however when R is plurality, m which may be the same or different is one or more integers)

[Formula 2]



(M is the basis chosen from the group of an alkaline metal and ammonium among a formula, however when M is plurality, n which may be the same or different is one or more integers.)

[Claim 2] said rustproof coating composition -- (\*\*) -- a compound and (\*\*) which have at least one phenolic hydroxyl group in a molecule -- compounds which have a siloxane skeleton

shown by a general formula (1), or those condensates, (b) a manufacturing method of the corrosion-resistant iron material according to claim 1 which is a rustproof coating composition which (\*\*) contains with the mixture ratio of 5:95-40:60.

[Translation done.]

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of corrosion-resistant iron material. It is related with the manufacturing method of high-corrosion-resistance iron material useful as iron material in which high corrosion resistance is demanded in a building material, construction machinery, a marine vessel, a craft, a bridge, a car, a vehicle, etc. in detail.

[0002]

[Description of the Prior Art] Rustproof processing of iron is widely performed from the former, and as these methods. Interception of oxygen by various paints, and water; inorganic covering; electrolytic protection, etc. which are represented by the chemical conversion by the covering; porcelain enamel; chromate salt and the phosphates by metal, such as nickel, copper, chromium, cadmium, zinc, aluminum, and tin, are put in practical use. As a high-corrosion-resistance processing method in case advanced rust prevention performance is required especially, especially, The iron-material surface is first covered with zinc or aluminum system metal, and it is considered as undercoat, it ranks second, and finishes by chromic acid system chemical conversion (chromate treatment), and the method of providing the protective layer by a paint if needed is put further in practical use. Although the processing by this chromium has a very high effect to rust prevention, the hexavalent chromium contained in the material used for chromate treatment is harmful to a human body, and since it becomes causes, such as liver incompetence, a skin ulcer, rhinitis, and asthma, it serves as a social problem in recent years.

[0003]

[Problem(s) to be Solved by the Invention] An object of this invention is to provide the manufacturing method of the corrosion-resistant iron material which has high rust prevention,

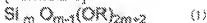
without using and containing a harmful chromium system compound.

[0004]

[Means for Solving the Problem]The purpose of above-mentioned this invention by a primer which uses as the main ingredients at least one sort of metal chosen from zinc and aluminum. A rustproof coating composition which uses the following (b) and (\*\*) as an essential ingredient is applied to the iron-material surface which covered the surface, and it is attained by forming a cured film by room temperature processing or heat-treatment.

(\*\*) a compound and (\*\*) which have at least one phenolic hydroxyl group in a molecule -- compounds which have at least one or more sorts of siloxane bonds chosen from a group of the silicate shown by a general formula (1), and the silicates which are shown by a general formula (2), and/or those condensates [0005]

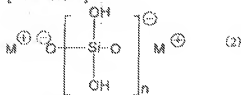
[Formula 3]



[0006](m from which R may be the same as or different among the formula when a hydrogen atom, the basis chosen from the group of the univalent hydrocarbon group, however R are plurality is one or more integers)

[0007]

[Formula 4]



[0008](n from which M may be the same as or different among the formula when an alkaline metal, the basis chosen from the group of ammonium, however M are plurality expresses one or more integers.)

[0009]

[Embodiment of the Invention]Rather than iron, the undercoat formed in the iron-material surface in this invention is a coat by the metal which uses as the main ingredients at least one sort of metal chosen from the big zinc and aluminum of the ionization tendency, and this coat metal serves as a sacrificial anode, and it can bar oxidation of iron material. The undercoat by these metal can be formed by a publicly known method like throats, such as spreading etc. of hot dipping, electroplating, osmosis plating, electroless plating and thermal spraying, and the paint that contains the fines of these metal further.

[0010]As a compound which has at least one phenolic hydroxyl group in the molecule of ingredient (b) in the rustproof coating composition used for this invention, Phenol, cresol, Timor, bromophenol, naphthol, Univalent phenols represented by anilinophenol etc.;

Pyrocatechin (catechol), The dihydric phenol represented by resorcinol, hydroquinone, orcin, urushiol, bisphenol A, binaphthol, etc.; although trivalent phenols; represented by pyrogallol, phloroglucine, hydroxyhydroquinone, trihydroxy benzoic acid, etc. is illustrated, It is not limited to these.

[0011]The compound which has at least one phenolic hydroxyl group in these molecules can be used, even if independent, or even if it mixes two or more sorts. These phenols react to iron, serve as iron salt, generate a complex compound, and since they reduce the permeability of oxygen, they can deter the zinc in undercoat, or oxidation of aluminum. As a result, since the performance degradation as a sacrificial anode of the above-mentioned metal in undercoat is controlled, it is thought that the high corrosion resistance over the long period of time of iron material is acquired.

[0012]A silanol group carries out dehydration condensation of ingredient (\*\*) used for this invention by desiccation, it forms a firm protection coat according to three-dimensional bridge construction, and supports ingredient (b) simultaneously.

[0013]The silicate shown by the formula (1) of ingredient (\*\*) is oligomer usually obtained by carrying out dehydration condensation of the alkoxide of silicon. Although not restricted about the structure of an alkoxide, and a molecular weight in particular, acquisition is easy, and the ethyl silicate obtained by the dehydration condensation of the methylsilicate obtained by the dehydration condensation of a tetramethoxy silane and a tetraethoxysilane has high reactivity, and it is suitable for it to use of this invention.

[0014]As silicates shown by the formula (2) of ingredient (\*\*), Although silicic acid amine, such as alkali metal salt, such as a lithium silicate, a sodium silicate, and a potassium silicate, methyl tripropanol ammonium silicate, and dimethyldipropyl ammonium silicate, etc. are illustrated, it is not limited to these.

[0015]Even if the compound which has a siloxane bond shown by these formulas (1) and a formula (2) is independent, or even if it mixes two or more sorts, it can be used. The compound which has a siloxane bond shown by these formulas (1) and a formula (2) can mix independence or two sorts or more, can perform a condensation reaction further, and can also use it as the amount object of polymers, and/or a co-condensation product.

[0016]What is necessary is for the rust prevention performance demanded just to determine the compounding ratio of ingredient (b) and ingredient (\*\*), and it is not limited in particular. however -- from the coating nature of this invention constituent, and a point of cured film intensity -- desirable -- weight mixture ratio (b):(\*\*) of ingredient (b) and ingredient (\*\*) -- 5:95-40:60 -- it is 10:90-20:80 still more preferably.

[0017]The above-mentioned rustproof coating composition can be applied to the iron-material surface covered with the primer which uses as the main ingredients at least one sort of metal chosen from zinc and aluminum by a spray, dipping, the brush, printing, etc. As dry membrane

thickness, although coverage is usually 5-200 micrometers, it is not limited to this. After applying the above-mentioned rustproof coating composition, it can dry at a room temperature for 2 to 10 hours, or it can be heated, and can obtain a cured film more in a short time. As heating conditions, it is heating of 10 minutes - 2 hours at 100-300 \*\*, for example, a desirable cured film can be obtained by heating at 150 \*\* for 30 minutes - 1 hour. The compound which has at least one phenolic hydroxyl group in the molecule which is ingredient (b) is fixed to the obtained coat, and the coat excellent in corrosion resistance is formed.

[0016]In the range which does not spoil the characteristic of this invention constituent, a proper quantity of other additive agents may be blended with the rustproof coating composition of this invention. Curing catalysts, such as a metal alkoxide added as other additive agents in order to harden early; The alcohols added in order to adjust viscosity, Diluting solvents, such as ketone and glycols; Glass, quartz, aluminium hydroxide, Inorganic bulking agents, such as alumina, kaolin, talc, calcium carbonate, a calcium silicate, and magnesium hydroxide; Acrylic resin powder, The colorant; metal-powder; lubricant; release agent; surface-active agent represented by paints and colors, such as organic bulking agent; carbon black, such as epoxy resin powder and polyester resin powder, red ochre, copper phthalocyanine blue, chromium yellow, and a titanium dioxide; although a coupling agent etc. are illustrated, it is not limited to these. The corrosion-resistant iron material furthermore manufactured by this invention can apply various paint and coating agents for the surface for protection, decoration, and the purpose to color.

[0019]

[Example]An example is raised to below and the typical example of this invention is explained still in detail. This invention is not limited by the following examples. That it is with a part only expresses a weight section among an example.

(Preparation of the constituent for glazing) The constituent (Examples 1-6, comparative examples 1-3) shown in Table 1 was prepared. Each raw material shown in Table 1 was paid to the Erlenmeyer flask in a predetermined quantity, and the constituent for glazing was prepared by filtering by the nylon mesh of 50 micrometers of openings after 30-minute agitation mixing at a room temperature. Raw material [ in front ] (A) - (F) is an ingredient as shown below.

(A) Methyilsilicate (MS-51 Mitsubishi Chemical, Inc.)

(B) Ammonium silicate (amine silicate QAS-25 Nissan Chemical Industries, Ltd.)

(C) Pyrocatechin (Kanto Kagaku, Inc.)

(D) 3,4,5-Trihydroxy benzoic acid ethyl ester (Kanto Kagaku, Inc.)

(E) Methyl trimetoxysilane (Wako Pure Chemical Industries, Ltd.)

(F) Tetraethoxy zirconate (Oiga Chicks ZA-60 Matsumoto Chemical Industry Co., Ltd.)

(G) 99.5% ethanol (Kanto Kagaku, Inc.)

[0020]

[Table 1]

項目	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	比較例 1	比較例 2	比較例 3
(A)	45 (鋼)	30	27	8	57	8	10	2	5
(B)	0	0	5	0	0	0	0	0	0
(C)	3	10	10	0	0	40	0	30	0
(D)	0	0	0	0	0	0	0	0	0
(E)	0	0	3	0	10	10	0	0	0
(F)	0	0	2	0	0	0	0	0	40
(G)	50	50	50	50	50	50	50	50	50

[0021](Preparation of a specimen) Zinc was applied so that coating weight might serve as the washing back by the shot-blasting method and might serve as 20 g/m<sup>2</sup> by a spraying process in the 25x100x2-mm steel plate surface. It pulled up to the constituent which shows this steel plate by which zinc processing was carried out in Table 1 after immersion for 10 minutes, dried to it at the room temperature for 30 minutes, it was dried in 150 more °C oven for 1 hour, and it was considered as the specimen.

(Neutral salt spray test) Continuation spraying of the salt solution was carried out 5% at one side of the prepared specimen, and the period to generating of rust on the surface of a steel plate was observed by viewing. Each examination used three specimens and observed time until generating which rusts on the surface about two specimens of them is accepted from the spraying start of a salt solution. The result was shown in Table 2.

[0022]

[Table 2]

試験片	錆び発生時間
実施例 1	1236 (時間)
実施例 2	1445
実施例 3	1518
実施例 4	1888
実施例 5	2012
実施例 6	1760
比較例 1	433
比較例 2	312
比較例 3	96

[0023]One to example 6 specimen prepared using the rustproof coating composition of this invention rusted, and a long time was remarkably proved at generating time as compared with the specimen of the comparative examples 1-3 so that clearly from the result shown in Table 2.

[0024]

[Effect of the Invention]the corrosion-resistant iron material manufactured by this invention is harmful -- high corrosion resistance is shown, without carrying out chromium compound content. Therefore, the iron material manufactured by this invention is suitable for members, such as a building material, construction machinery, a marine vessel, a craft, a bridge, a car,



and a vehicle.

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[Translation done.]